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STRUCTURAL ASPECTS and SURFACE PROPERTIES MOLYBDENUM /COMPOSITE OXIDE CATALYTS

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ABSTRACT

Molybdenum / composite oxide catalysts play an important role in dehydrogenation – hydrogenation process. In the present investigation, alumina-magnesia and alumina-chromia composite materials were used as supports. The structural and phase changes of the prepared catalysts were determined using different techniques: Fourier transform infrared spectroscopy, x-ray diffraction pattern, differential scanning calorimetry and surface properties. X-ray diffraction pattern exhibited the formation of $MgMoO_4$ phase on the surface of alumina-magnesia support with small crystallite size. Bulky crystallites $Cr_2(MoO_4)_3$ were formed on alumina-chromia support. The thermal decomposition data confirmed the formation of MoO_2 (200-230°C), $Cr_2(MoO_4)_3$ (230-280°C), MoO_3 (400-450°C) and $MgMoO_4$ (450-550°C) phases. Surface properties indicate that, the bulky crystallites formed on the surface of alumina-chromia support, caused blocking of its pores and led to a significant decrease in surface area from 240.2 m²/g for Mo/alumina-magnesia to 91.04 m²/g for Mo/alumina-chromia catalyst.

KEYWORDS:

Molybdenum, Support, Catalyst, Alumina, Magnesia, Chromia Composite mixed oxides.

INTRODUCTION

Molybdenum supported on alumina was used in many industrial processes such as dehydrogenation –hydrogenation, and reforming processes. Molybdenum was conventionally prepared by pore volume impregnation [1] of dried alumina with molybdate solution that interacted with protonated hydroxyls and hydroxyl groups[2].

One way to improve the catalytic performance of molybdenum catalyst was to increase the amount of active phase on the carrier. Unfortunately, the major drawback of the conventional incipient wetness impregnation [3] was that the amount of molybdenum introduced was limited by its solubility in the impregnation solution and the volume of which was restricted by the total pore volume of alumina. To increase the amount of molybdenum deposited onto the carrier, the successive incipient wetness impregnation could be used but this did not appear appropriate. Therefore, a more interesting solution may consist of using supports that having high surface area.

It has been reported that high specific surface area molybdenum oxycarbide could be prepared from oxidative treatment of high surface area Mo_2C or low surface area MoO_3 [4,5]. Daturi et al., [6] showed that Mo/SnO_2 catalyst was very active catalyst for the oxidative dehydrogenation of alcohols; it showed higher activity than Mo/TiO_2 , $\text{Mo}/\text{Al}_2\text{O}_3$ and Mo/SiO_2 catalysts.

Mixed oxide supports showed also high surface area and peculiar behavior compared to the original pure oxides. This may be due to the combination of dissimilar components in the same molecular network structure. Cadus et al., [7] prepared molybdenum supported on alumina-magnesia mixed oxide and found that, MgMoO_4 system provided high selectivity to propene. It has been pointed out that, a slight excess of MoO_3 was necessary to make the catalyst an active one. Armaroli et al., [8] explored an alternative way to prepare $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst by impregnation of molybdenum onto boehmite and then transformed it to $\text{MoO}_3/\text{alumina}$, the catalyst showed high surface area.

Kumar et al., [9] prepared a series of molybdenum loading from 2 to 14 wt% on $\text{MgO}-\text{Al}_2\text{O}_3$ mixed oxide by incipient wetness impregnation. The results indicated that, the presence of MoO_3 species further enhanced the acidity of catalyst favorable for hydrocracking. Some authors demonstrated that magnesium molybdate exhibited higher selectivities toward olefin formation compared with magnesium vanadate systems. Each of these described an improvement in the catalytic activity of MgMoO_4 with slight excess of molybdenum species [10, 11].

Several molybdenum containing hydrotalcite like compound were prepared by different ionic exchange procedure using as parent synthetic hydrotalcite. The catalysts showed higher activity towards hydroperoxidation [12].

This work investigates the nature of molybdenum species on previously prepared alumina; alumina-magnesia and alumina-chromia composite mixed oxides. Emphasis was placed on the physicochemical characterization of the prepared catalysts with the aim of studying the nature of active sites and surface properties.

EXPERIMENTAL

Preparation of Catalyst

γ - Alumina, alumina-magnesia and alumina-chromia [previously prepared via co-precipitation technique and followed by calcination at 450°C for alumina and alumina-magnesia & at 600°C for chromia-alumina] were impregnated with ammonium heptamolybdate solution at pH ~ 12 using ammonium hydroxide to prepare the corresponding catalysts. The prepared catalysts dried at 120°C and then calcined in presence of flow of purified air. The calcination was performed in two steps, firstly from ambient temperature to 450°C and maintained at this temperature for two hours and then calcined at 600°C for six hours. The amount of ammonia heptamolybdate was equivalent to 20wt% MoO₃ loading [13].

Structural Phase changes

The prepared catalysts were characterized by applying different techniques as; Fourier transform infra red spectroscopy, to identify the hydroxyl and the functional groups in the catalysts. X-ray diffraction pattern, to study the crystalline phases and the crystallite size using Sherrer's equation. Differential Scanning Calorimetry was studied to identify the different oxide phases formed upon thermal treatment. In addition, nitrogen physisorption isotherms were measured to calculate the surface area from adsorption curve by BET method.

Surface Acidity

A Boehm's base neutralization technique [14] was used for measuring the surface acidity of the prepared catalysts. In this technique, 0.2 gm of sample was mixed with 100 ml of 0.1N NaOH solution and maintained overnight at room temperature. The mixture left to settle then filtered. The excess base (NaOH) was back titrated with standard solution of 0.1N HCl and the acidity was calculated from this equation:

$$\text{Acidity (meq/100gm)} = (a-b) \cdot 100/1000 \cdot N \cdot 100/0.2,$$

Where:

- a = ml HCl in blank for 10 ml NaOH ,
- b = ml HCl equivalent to 10 ml of sample filtrate,
- N = normality of NaOH.

RESULTS and DISCUSSION

FT-IR Spectroscopy

FT-IR spectral analysis for alumina, molybdenum/alumina and thermally treated molybdenum/alumina, molybdenum/alumina-magnesia & molybdenum/ alumina-chromia catalysts were run on Perkin Elmer FT-IR apparatus. The spectrum recorded at range from 1200-500 cm^{-1} and extended FT-IR spectrum at 3800-3200 cm^{-1} . Data in Figure (1-a) reflected the appearance of a band at 1050 cm^{-1} typical for γ -alumina due to Al-O vibration mode in addition to five bands in the OH stretching region 3800-3400 cm^{-1} : a weak shoulder band at 3790 cm^{-1} related to the terminal OH over one tetrahedrally coordinated aluminum ion in non vacant environment, band appeared at 3775 cm^{-1} ascribed to the terminal OH over one tetrahedrally coordinated aluminum ion near a cation vacancy. Band appeared at 3735 cm^{-1} related to terminal OH over one octahedrally coordinated Al ion, band appeared at 3670 cm^{-1} related to the bridging OH, band at 3590 cm^{-1} related to the triply bridging OH and band at 3570 cm^{-1} assigned to stretching modes of physisorbed water[15,16].

Figure (1-b) ascribed one broad band, at 970 cm^{-1} , that could be observed for molybdenum/alumina catalyst. Molybdenum dispersed species i.e., surface polymolybdate and isolated hydrated tetrahedral species showed band at 970 cm^{-1} attributed to Mo=O vibrations[17,18]. Even if these species were intrinsically different, the nature of the Mo=O bond is the same, which resulted in appearance of bands with similar wave numbers. Band appeared at 3210 cm^{-1} typical for N-H bond vibration due to ammonium salt used during the preparation. Moreover, acidic hydroxyl group for γ -alumina appeared at 3775 cm^{-1} while a band at 3670 cm^{-1} (most basic hydroxyl group) was not observed. These bands ensure the complete interaction of molybdenum species with basic alumina hydroxyl groups. This also indicated that, support acquired negative charge of the impregnated ammonium heptamolybdate solution that enhanced their adsorption affinity toward positively charged Mo^{+6} ions and thus their high dispersity in support [20].

For calcined molybdenum/alumina catalyst (Fig.1-c), new bands were appeared at 860 and 1005 cm^{-1} . The vibration at 860 cm^{-1} may be associated with Mo-O-Mo or due to Mo-O-Al bonds. According to Kasztelan et al. [1] assignment, the appearance of band at 860 cm^{-1} for Mo/ Al_2O_3 catalyst was due to Mo-O-Al bond vibrations in this region. Actually, band at 1005 cm^{-1} could be attributed to crystalline MoO_3 [17]. These bands are associated the vibration of Mo=O in MoO_3 phase and Mo-O-Al in aluminum molybdate phase. Whereby, the disappearance of bands at 970 and 3210 cm^{-1} accompanied the decomposition of ammonium heptamolybdate upon thermal treatment.

For calcined molybdenum/ alumina-magnesia catalyst, band appeared at 910 cm^{-1} ascribed to magnesium molybdate, in addition to band assigned to MoO_3 species (1005 cm^{-1}) (Fig1-d). The spectrum for calcined molybdenum/ alumina-chromia catalyst in Fig.(1-e) showed the appearance of band at 900 cm^{-1} , assigned to vibration of Mo-O-Cr in molybdenum dichromate and or in chromium molybdate, in addition to MoO_3 band. Band appeared at 1115 cm^{-1} could be due to bulk

tetrahedrally Al-O stretching of α -alumina. In addition, band appeared at 3740 cm^{-1} related to bridged OH group and terminal octahedral OH group with vacancy and this is typical for α - alumina. The presence of chromia species facilitated transformation of γ - form to α - one at lower temperature "600°C" via sintering effect according to El-Shobaky et al., [21].

X-ray Diffraction Pattern

X-ray diffraction analysis (XRD) for all catalysts was carried out using XD-D1 – x-ray diffraction Shimadzu apparatus and the data depicted in the Figs. (2-4).

For molybdenum/alumina catalyst, the diffractogram in Fig.2-a, revealed the appearance of broad peaks characteriz γ - alumina at d – spacing 2.41, 1.98 and 1.40 Å, (ASTM 04-0875). Molybdenum species in ammonium heptamolybdate detected at d- spacing: 3.85, 3.11 and 1.85 Å [13,22]. Figure (2-a) revealed the appearance of a line at d-spacing: 3.11 Å with low intensity, the other lines may be shielded upon incorporation of molybdenum species inside alumina pores. Diffractogram for calcined molybdenum/alumina-magnesia (Fig. 2-b), exhibited broad peaks at d-spacing 6.91, 3.09 and 2.41 Å related to the formation of $\text{Al}_2(\text{MoO}_4)_3$ phase [13].

For molybdenum/alumina-magnesia catalyst (Fig.3a), lines are detected at d-spacing 2.43, 2.02 and 1.42 Å characteristic for alumina-magnesia composite [22], in addition to the lines that related to molybdenum species. After thermal treatment, x-ray diffraction pattern in Fig.3-b, revealed the appearance of lines at d-spacing 3.39, 2.08 and 1.43 Å which could be due to the presence of MgMoO_4 [13]. Thus, it seems that molybdenum reacted preferably with magnesia component of the support and formed very stable crystallites of MgMoO_4 . These species were large crystallites, which accounted for their XRD peaks. The broadening of the peaks suggested that magnesium molybdate was distorted.

For molybdenum/ alumina-chromia catalyst (Fig.4-a), lines detected at d-spacing : 3.65, 2.66 and 1.69 Å corresponded to Cr_2O_3 phase [23] and that detected at d-spacing : 3.59, 2.63 and 1.79 Å corresponded to α - alumina [24], in addition to that other lines were detected, indicating the presence of molybdenum species (d-spacing: 3.85, 3.11 and 1.58 Å) . Diffractogram for calcined molybdenum/alumina-chromia catalyst (Fig. 4-b), showed new lines at d-spacing: 7.43, 5.88 and 2.93 Å correspond to $\text{Cr}_2(\text{MoO}_4)_3$ phase[25] . Moreover, lines detected at d-spacing: 5.01, 5.23 and 4.77Å assigned to MoO_2 phase [26]. Also, lines were detected at 10.57, 3.27 and 2.28 Å related to MoO_3 phase and that at d-spacing: 6.91, 3.09 2.41 Å related to $\text{Al}_2(\text{MoO}_4)_3$ phase formation [13].

Crystallite size

Crystallite size data for the prepared catalysts before and after calcination were included in Table (1). Data indicated that, the crystallite size had relatively low values (7.0, 10.6 nm) for molybdenum/alumina–magnesia catalyst. This may be due to the presence of relatively smaller particles of magnesia compared with competitive alumina particles that allowed the dispersion of molybdenum species and consequently prevented their aggregation.

On the other hand, the crystallite for molybdenum/alumina-chromia catalyst, showed high values (47.0 and 44.9 nm). This high value could be due to the presence of large acidic Cr_2O_3 (2Cr^{+3} 3O^{-2}) species which induced attractive forces between the different particles and permitted the aggregation of molybdenum species.

After thermal treatment, the crystallite size data showed the same trend as that obtained for the previous prepared catalysts. This confirmed that alumina-magnesia support prevented the formation of large molybdenum oxide particles and facilitated the dispersion of the formed magnesium molybdate phase on its surface, as clarified from XRD data. Concurrently, for calcined molybdenum/alumina-chromia, different chromium-molybdenum phases were formed on the surface of alumina-chromia support, these species were migrate and agglomerate together to form bulky crystallites of size 38.5 and 86.5 nm.

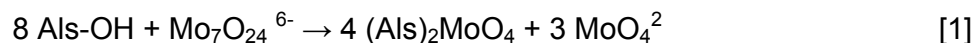
Base Neutralization

Applying Boehm's base neutralization technique [14] for measuring the surface acidity of the prepared molybdenum catalysts, data were included in Table (2). Data clarified that the alumina-magnesia support exhibited the lowest value compared with the other two supports. For the corresponding catalysts, the same trend was observed. In other words, molybdenum/alumina-magnesia catalyst was the lowest one and the catalyst having the highest surface acidity was molybdenum/alumina-chromia as follows:

Support: Alumina-magnesia < alumina < alumina-chromia
 Catalyst: Molybdenum/alumina-magnesia < Molybdenum/alumina < Molybdenum/ alumina-chromia

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was carried out using the Differential Thermal Analyzer, Perken Elmer apparatus; the profiles for the prepared catalysts were represented in Fig (5). For molybdenum/alumina catalyst (Fig.5-a), three endothermic peaks appeared, the first at temperature range 100-120°C related to the removal of surface adsorbed water. The second peak appeared at temperature range 400-450°C related to the decomposition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \rightarrow 7\text{MoO}_3$ producing the corresponding oxide form [20]. The last one at 550-600°C correspond to the formation of aluminum molybdate phase. The heat of absorption (enthalpy) for this peak had low value 3.87 $\mu\text{V}\cdot\text{s}/\text{mg}$ (Table 3), that indicated the easiest formation of polymolybdates species on the surface of amphoteric alumina support with its abundant OH groups.



An exothermic peak appeared at temperature range 950-1000°C, related to transformation of γ -alumina to α -form [1].

For molybdenum/ alumina-magnesia catalyst, DSC profile (Fig.5-b) revealed a new endothermic peak in addition to the surface adsorbed water, MoO_3 and aluminum molybdate phase peaks. This peak appeared at temperature range 380-450°C could be related to the formation of magnesium molybdate [22], which co-existed with aluminum molybdate on the catalyst surface.

It is well known that, alumina-magnesia support contained abundance of basic hydroxyl groups, that allowed depolymerization of polymolybdate anion occurred yielding monomeric species anchored to the oxide surface. The formation of ammonium mono-molybdate can be represented as follow:

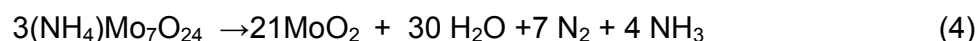


under further heating, decomposition of ammonium mono-molybdate occurred with formation of ammonia:



As shown, strong base (MgO) replaced a weak one (ammonium species) in a molybdate salt and then basic OH group stabilized the highest Mo^{6+} oxidation state (MgMoO_4). MgO is a strong basic support, high local pH of this support led to depolymerization of polyoxomolybdates [27]. So most tetrahedral MoO_4 moieties believed to be present in this catalyst, as confirmed from the enthalpy values "4.67" for formation of magnesium molybdate species and "6.72 $\mu\text{V.s/mg}$ " for aluminum molybdate ones (Table 3).

For molybdenum/ alumina-chromia catalyst, four endothermic peaks appeared in addition to the surface water adsorption peak. The first at temperature range 200-230°C assigned to well crystallized MoO_2 that formed on auto reduction of ammonium salt occurred probably according to the following reaction [27, 28].



The second and third endothermic peaks appeared at 230-280 and 280-380°C related to formation of chromium and aluminum molybdate respectively. The fourth one at 420-500°C related to formation of MoO_3 phase. As known, acidic support facilitated the formation of MoO_3 bulk like particles beside the MoO_3 clusters and polymolybdate species [27]. Enthalpy values were parallel to this behavior and showed a low values for the formation of these different oxide phases. As clarified, the temperature of ammonium heptamolybdate decomposition on alumina-chromia support was lower than that on alumina – magnesia one. This may be due to the presence of chromia species which hasten the decomposition of ammonium heptamolybdate at lower temperatures. The mass loss was accompanied by the endothermal effects as shown in the thermogravimetric curve (TG, Fig. 5). This loss

in weight resulted from the evolution of ammonia and H-bonded water that may either be attached to already adsorbed water molecule or to surface hydroxyl groups.

Surface Area and Pore Structure

Nitrogen isotherms were measured using Quantachrome Noava Automated Gas Sorption apparatus. Full nitrogen adsorption-desorption isotherms were obtained for molybdenum/alumina catalyst and that produced after thermal treatment of, molybdenum/alumina, molybdenum/alumina-magnesia and molybdenum/ alumina-chromia ones. Specific surface area (S_{BET}), total pore volume (V_p), mean pore radius (r_H), BET-C constant and fraction of micro porosity (m_f %) data were included in Table (4).

All samples showed type IV isotherm of the Brunauer classification with H2 hysteresis loop according to IUPAC classification [29]. This kind of hysteresis loop is an indication of a network of interconnected pores with narrower parts (Fig.6). The S_{BET} values for the calcined catalysts were computed from linear plots of the S_{BET} equation. The adsorption isotherm for molybdenum/alumina catalyst (Fig.6-a) showed small hysteresis and this could result from the formation of bulk crystallites attacked the pores of alumina, blocked some of narrower pores and also attacked the walls of the wider ones, giving rise to smaller surface area, pore volume and narrower pores. Thermal treatment at 450°C for molybdenum/alumina catalyst, produced an increase in, S_{BET} (from 24.95 to 133.6 m²/g), pore volume (from 0.01316 to 0.0713 cc/g), average pore radius (from 0.8016 to 1.4 nm) and microporosity % (from 9.9 to 16.87%). Such increase arises from the decomposition of incorporated ammonium heptamolybdate into smaller molybdenum-oxygen entities with the removal of ammonia that produced the observed changes.

For molybdenum/alumina-magnesia catalyst calcined at 600°C, a further increase in surface area was observed from 133.6 for calcined molybdenum/alumina to 240.2 m²/g. This increase indicated the modification of alumina-magnesia structure resulted from the interaction with molybdenum and formation of new oxide phases, in agreement with XRD and DSC data. This interaction is responsible for the creation of new pores that contributed to the increase in surface area. The increase in pore volume from 0.0713 to 0.188 cc/g, ensure a deeper penetration of the formed phases inside pore system that was enhanced due to the increase in surface interactions. Some accumulation of the formed species on pore walls could be concluded from the slight decrease in average pore radius from 1.4 to 1.05 nm and from 16.87 to 13.80 %, for m_f % (Table 4).

Concurrently, for molybdenum/ alumina-chromia catalyst calcined at 600°C, surface area showed a low value 91.04 m²/g. This related to formation of bulk crystallites of chromium and molybdenum oxide phases that covered different sites on the catalyst surface causing a blockage of pores and a decrease in surface area. In addition, the decrease in pore volume with the increase in m_f % (as compared with molybdenum /alumina-magnesia catalyst) is related to: these bulk crystallites densely accumulated on support pore walls to diminish its radius and consequently the calculated microporosity % was shown to be high (Table 4).

Nickolov et al., [30] reported that, Mo-O entities are formed as tetrahedral monomeric MoO_4 and or octahedral polymeric $-\text{[MoO}_6\text{]}_n$ surface species that interacted with chromium species formed bulk crystallites, in addition to bulk MoO_3 crystallites that caused semi blocking of alumina pores and provoked a decrease in surface area.

V_t-t Plot

To analyze the isotherm of materials containing micro- and mesoporosity, t-method of de Boer et al., [29] was applied. The obtained S_t values showed fair agreement with the corresponding S_{BET} values indicating a suitable choice of t-curves on the basis of the BET-C constant. For molybdenum/alumina catalyst, V_t -t plot (Fig.7) showed downward deviation at $t > 0.8\text{nm}$, thus the material is a microporous one, but $m_f\%$ has low value (Table 4). This situation is a result of blocking and accumulation of ammonium heptamolybdate species inside alumina pores that caused a decrease in V_p and r_H values and a sharp decrease in surface area was observed. In addition to that, a very low adsorption value (Fig.7) was observed, this could be due to the blocking of most of micropore with ammonium heptamolybdate species and their accumulation inside alumina mesopores which left small size of pores to measure. Thus, the downward deviation was not a result of formation of micro pores as observed by small value of $m_f\%$. After calcination, the material showed upward deviation as a result of destruction of the ammonium heptamolybdate blocking the pores and the removal of ammonia, in addition to the electrostatic repulsion created by charge adsorbed at the surface of particles. These two factors create an intracrystalline microporosity as indicated from the increase in $m_f\%$ and pore volume.

Calcined molybdenum/alumina –magnesia catalyst (Fig.7) showed also an upward deviation (capillary condensation) characteristic for mesoporous materials at $t > 0.8\text{nm}$ with high value of adsorbed volume. The slight decrease in $m_f\%$ and average pore radius and the increase in pore volume suggested the generation of new deeper and slight wide pore that implies the dispersion of molybdenum species on support.

Calcined molybdenum/alumina-chromia catalyst showed an upward deviation at $t > 0.6\text{ nm}$ but with a relatively low value of adsorbed volume. The decrease in V_p , r_H could be explained by the aggregation of molybdenum inside support. Consequently, the increase in $m_f\%$ suggested the shrinkage of many crystals during calcination which did not create internal porosity.

CONCLUSION

From the results shown above, it could be concluded that the preparation of Mo catalysts using different composite oxide supports allowed the formation of different phases as established using different techniques:

- X-ray diffraction pattern detected the formation of Mg MoO_4 active sites on alumina-magnesia support. This phase characterized by its small crystallite size. Bulky crystallites of different molybdenum-chromium oxide phases were formed on alumina-chromia support.

- Differential scanning calorimetry analysis suggested that the support chemistry was responsible for the decomposition of ammonium heptamolybdate, consequently on alumina- magnesia support, the presence of basic MgO facilitate its decomposition and formation of magnesium molybdate. On the other hand, its decomposition on alumina-chromia support (Cr_2O_3 is acidic support) caused formation of bulk MoO_3 , polymolybdate species and well crystallized MoO_2 that were formed on auto reduction of ammonium salt.
- Surface properties established that, the surface area of molybdenum/alumina-magnesia catalyst was the highest compared with the other prepared catalysts.

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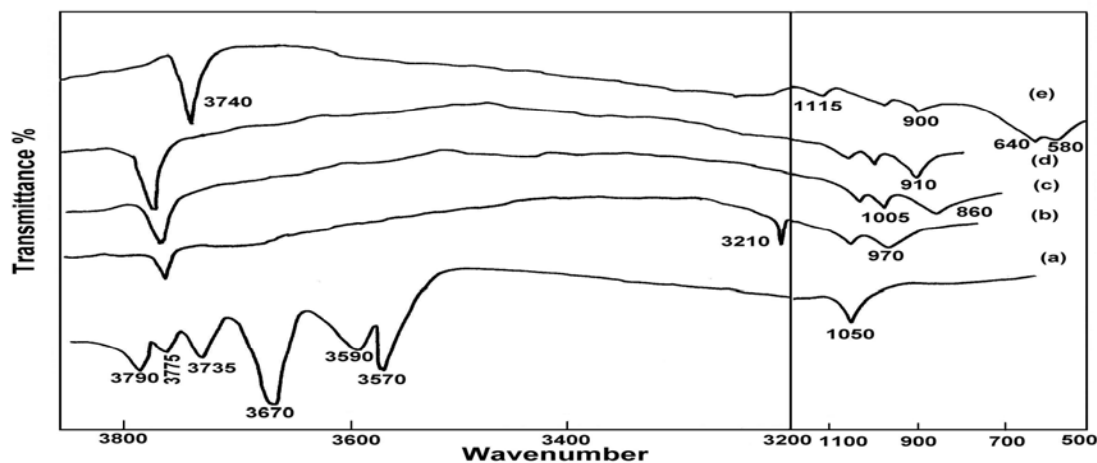


Fig. (1): FT-IR Spectra of: (a) γ -alumina (b) Molybdenum/alumina (c) Molybdenum/alumina* (d) Molybdenum/alumina-magnesia* (e) Molybdenum/alumina-chromia*

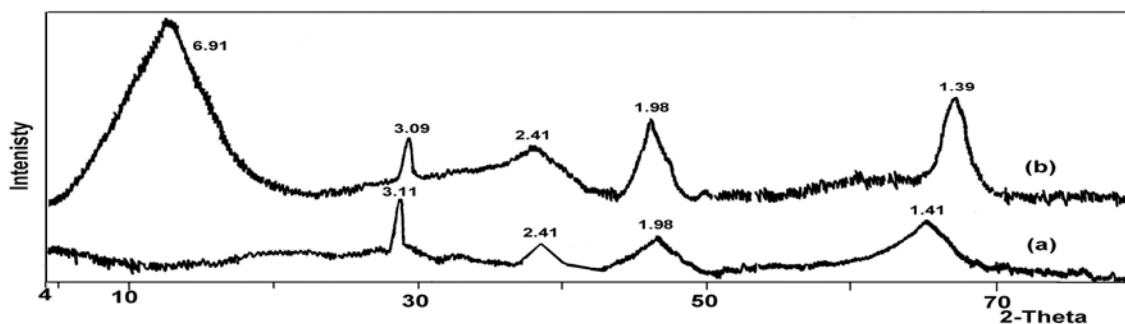


Fig.(2): X-ray Diffraction Pattern of: (a) Molybdenum/alumina (b) Molybdenum/alumina*

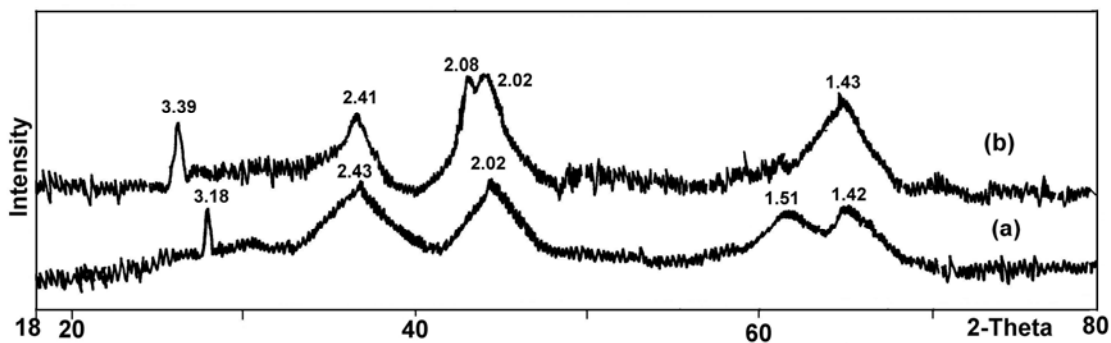


Fig. (3): X-ray Diffraction Pattern of: (a) Molybdenum/alumina-magnesias (b) Molybdenum/alumina - magnesias*

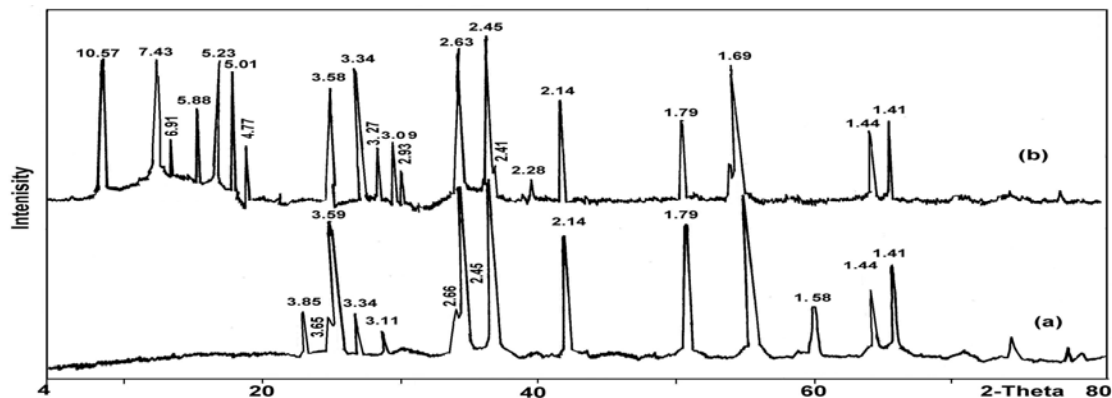


Fig.(4): X-ray Diffraction Pattern of: (a) molybdenum/alumina-chromia
(b) molybdenum/alumina – chromia*

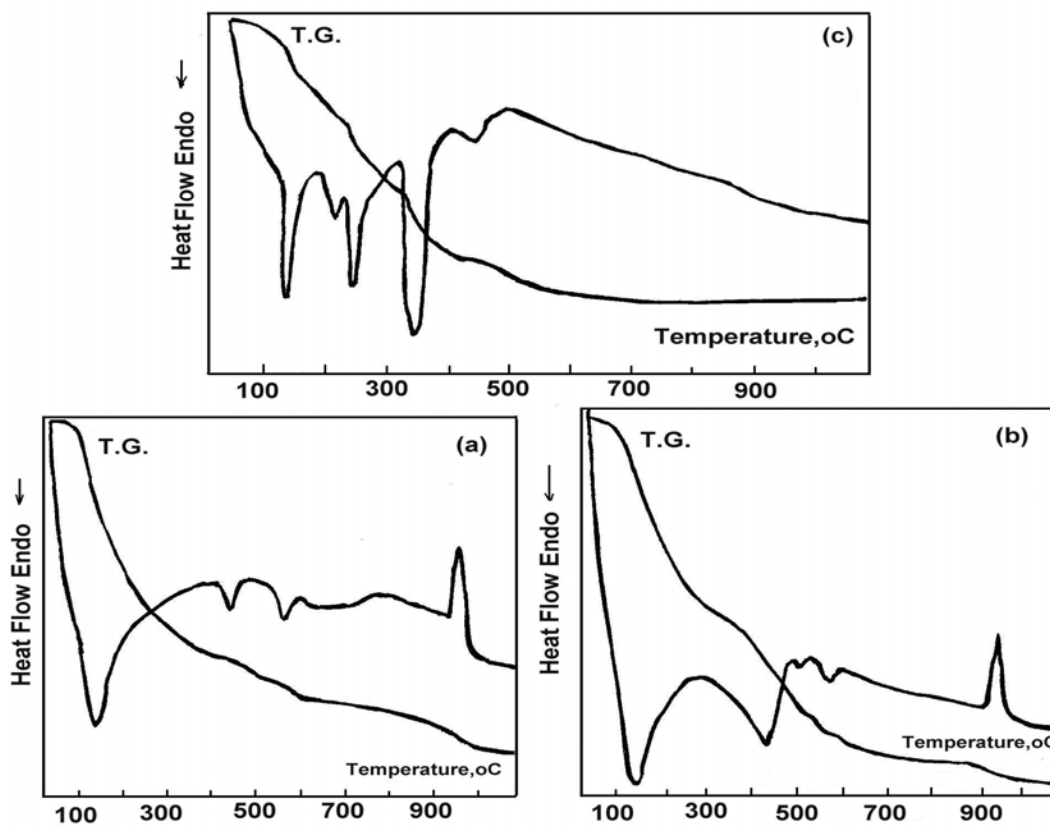


Fig. (5) Differential Scanning Calorimetry Profiles for: (a) Molybdenum/alumina
(b) Molybdenum/alumina-magnesia (c) Molybdenum /alumina-chromia

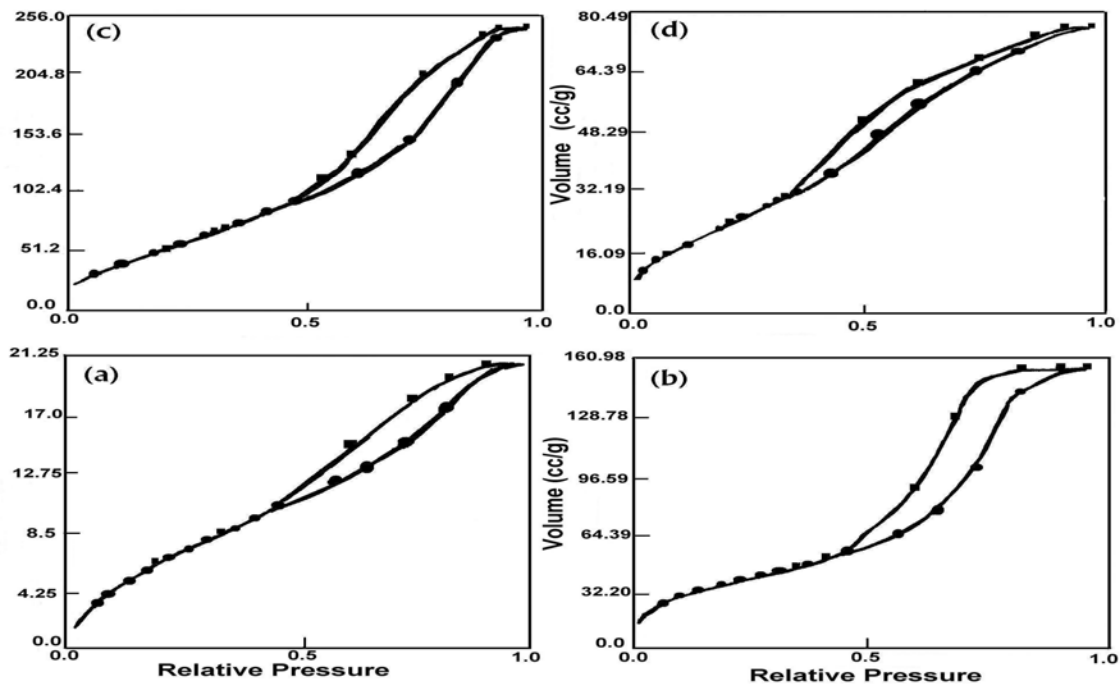


Fig. (6) :N₂ Adsorption Isotherm of : (a) Molybdenum/alumina(b) Molybdenum/alumina*

(c) Molybdenum/alumina – magnesia*

(d) Molybdenum/alumina – chromia*

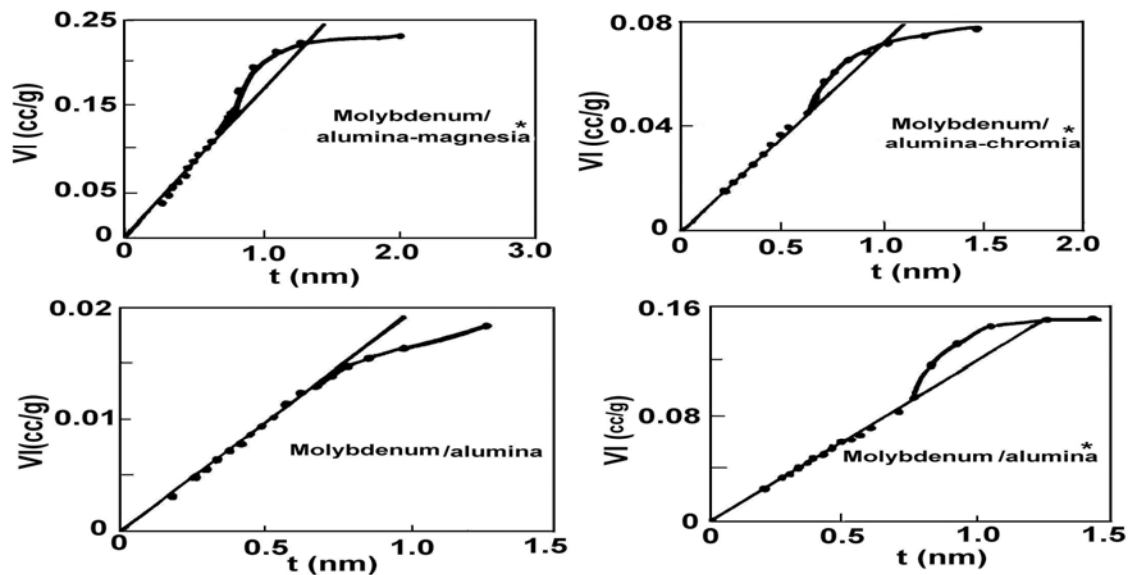


Fig.(7): V_t-t Plot for the Prepared Catalysts

Table (1): Crystallite Size for Prepared Molybdenum Catalysts.

2θ	Mo/alumina	Mo/alumina-magnesia	Mo/alumina-chromia
28.9	36.89	----	-----
36.79	23.36	7.00	47.00
41.9	----	-----	44..90
44.79	----	10.60	-----
2θ	Mo/alumina*	Mo/alumina-magnesia*	Mo/alumina-chromia*
36.6	28.26	6.1	38.5
41.97	----	----	86.5
45.6	19.2	4.9	----

Table (2): Surface Acidity for Prepared Molybdenum Catalysts.

Sample	Al ₂ O ₃	Al ₂ O ₃ -MgO	Al ₂ O ₃ -Cr ₂ O ₃	Mo/Al ₂ O ₃ *	Mo/Al ₂ O ₃ -MgO*	Mo/Al ₂ O ₃ -Cr ₂ O ₃ *
Acidity (meqv1100.gm ¹)	22.3	8.5	26.0	27.0	14.7	33.5

Table (3): Thermal Analysis of Molybdenum Catalysts.

1-Molybdenum/alumina

Temperature°C	Type of peak	Enthalpy μV.s/mg	Weight loss%
100-120	Endo-thermic	28.93	12.92
400-450	Endo-thermic	3.68	3.24
550-600	Endo-thermic	3.87	9.15
950-1000	Exo-thermic	-0.71	2.69

2-Molybdenum/alumina-magnesia

Temperature°C	Type of peak	Enthalpy μV.s/mg	Weight loss%
100-120	Endo-thermic	13.62	10.25
380-450	Endo-thermic	4.67	10.39
400-450	Endo-thermic	6.72	1.18
550-600	Endo-thermic	16.72	2.01
950-1000	Exo-thermic	-0.42	1.77

3-Molybdenum/alumina-chromia

TemperatureoC	Type of peak	Enthalpy μV.s/mg	Weight loss%
100-120	Endo-thermic	13.33	12.92
200-230	Endo-thermic	0.67	5.56
230-280	Endo-thermic	6.72	13.71
280-380	Endo-thermic	26.06	17.62
420-500	Endo-thermic	0.84	6.81

Table (4): Surface Properties of the Prepared Catalysts

Catalyst	BET constant	S _{BET} (m ² /g)	S _t (m ² /g)	V _p (cc/g)	r _H (nm)	m _f (%)
Alumina	65.04	170.8	164.54	0.0948	1.187	13.85
Mo/Alumina	28.06	24.95	15.64	0.01316	0.8016	9.90
Mo/Alumina*	104.1	133.6	115.93	0.0713	1.4	16.87
Mo/Alumina-Magnesia*	120.86	240.2	236.31	0.188	1.050	13.80
Mo/Alumina-Chromia*	49.11	91.04	81.57	0.0507	0.8316	18.24

*calcined catalysts